ISBN 978 – 979-98623-1-0

REACTION KINETICS OF MAGNESIUM COMPOUND RECOVERY FROM BITTERN USING SLAKED LIME CONTINOUSLY

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Abstract

Bittern containing magnesium compounds, is quite a lot, but up till now it is just wasted. On the other hand, Indonesia needs a great deal of magnesia bricks. Therefore, this research was intended to recover magnesium from the bittern in the from of magnesium hydroxide in a baffle reactor continuously using counter current flow

The process was carried out by feeding slaked lime from the top, while bittren and air from the bottom of the reactor. After 20 minutes of operation liguid samples were taken at 10 minutes intervals until steady state condition was reached. This was indicated by constant values of pH and magnesium concentration. The process was continued for 10 – 20 minutes more to ascertain that steady state condition was really at tained. The magnesium ions in the samples was determined volumetrically. In this research, the variables studied included air flow rate, temperature, equivalent ratio of $Ca(OH)_2$-$MgCl_2$, and the initial concentration of magnesium chloride in the bittren.

Based on the effects of air flow rate and temperature, the rate of Mg(OH)z formation was controlled by chemical reaction. Within the range of the variables studied, the reaction rate constant was affected by temperature exponentially, while air flow rate, $Ca(OH)_2$-$MgCl_2$ equivalent ratio, and initial magnesium chlorlde concentrations showed logarithmic relations with k. The relative favourable process conditions were found to be air flow rate of 281 mL/min, temperature of 29 C^o $Ca(OH)_2$-$MgCl_2$ equivalent ratio of 3, initial magnesium chloride concentration of 0,34mgnol/mL. Under these conditions, the conversion of MgCl2 was 89,17 %.

***Keywords**: bittern – magnesium hydroxide – kinetics.*

1. INTRODUCTION

Magnesium compounds widely used for industrial heat-resistant bricks. Until now, Indonesia still bring in magnesium compound from abroad amounting to 27,565 tons in 1992 (BPS, 1992). For that purpose it required considerable foreign exchange. In Indonesia there are actually many bittern (salting the mother liquor) containing magnesium ions of about 50 grams / liter, but until now the liquid was just thrown into the sea.

Collection of business people as a magnesium salt of the batch has been done, by adding lime goes into people's salt solution which is accompanied by stirring and heating (Istiawan et al, 1985). To pick up magnesium from bittern in the form of magnesium hidroksid, added lime and the process runs out in the reactor is tilted upright berpenghalang with the principle of continuous countercurrent. If this study worked well and further developed in the industry, imports of magnesium compounds can be reduced and the bittern is wasted can be utilized.

The reaction liquid with a grain of solids in the reactor pipe sloping berpenghalang has been done by previous research. Izidin (1993) to the manufacture of aluminum sulfate from water Prone Ijen and bauxite are continuous inside the reactor pipe berpenghalang jagged oblique, along with air bubbles as a stirrer. Conversion of the formation of aluminum sulfate to 90% with a purity of 94.7%. Decisive step is the chemical reaction and the reaction mechanism follows the theory of Shrinking Core Model.

The reaction between MgCl 2 in bittern with Ca (OH) 2 in lime outages are:

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2 \quad (1)$$

For plug flow stream, the reaction velocity equation is:

$$-rA = \frac{C_A}{\frac{1}{k_L a_s} + \frac{1}{k_s a_s} + \frac{1}{k_r a_s}} \quad (2)$$

Based on equation (2), the overall speed is determined by the diffusion resistance in liquid-solid layer, $(k_L)^{-1}$, the solid-solid layer $(k_s)^{-1}$, and the barriers of chemical reactions, $(k_r)^{-1}$

Reaction rate equation for the liquid magnesium chloride:

$$-r_A = -\frac{dC_A}{d\tau_A} \quad (3)$$

And the reaction rate equation for the solid calcium hydroxide:

$$r_B = \frac{dC_B}{d\tau_B} \quad (4)$$

CB value is calculated by:

$$C_B = \frac{N_{rt}}{V} \rho_B \; V_B \quad (5)$$

If equation (5) inserted into equation (4), and N_{rt}/V, and P_B are considered fixed and the value of $V_B = \frac{4}{3}\pi R^3_B$, obtained:

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$$-r_B = \frac{N_{rt}}{V} \rho_B 4\pi R^2_B \frac{dR_B}{d\rho_B} \quad (6)$$

Based on equation (1):

$$-r_A = -r_B \quad (7)$$

The relationship between τ_A and τ_B are considered straight-line:

$$\tau_A = a + b\,\tau_B \quad (8)$$

When equation (8) in the differential, will be obtained:

$$d\tau_A = b\,d\tau_B \quad (9)$$

Substitution of equation (3), (6), (7), and (9) into equation (2), gives the result:

$$-\frac{dR_B}{d\tau_A} = \frac{C_A}{4\pi \frac{N_{rt}}{V} \rho_B R_B \left[\frac{1}{k_L k_s} + \frac{1}{k_s a_s} + \frac{1}{k_r a_s}\right]} \quad (10)$$

For a small grain size of solids and large diffusivity values, the mass transfer coefficient according to Ranz and Marshall (Levenspiel, 1972) form:

$$k_L = \frac{2D}{dp} = \frac{D}{R_B} \quad (11)$$

The relationship between the radius of grain solids with solids conversion are:

$$R_B = R_o (1-x_B)^{1/3} \quad (12)$$

If equation (12) substituted into equation (11), is obtained:

$$k_L = \frac{D}{R_o(a_o + XB)^{1/s}} \quad (13)$$

Inserting equation (3) and (13) into equation (2), provides:

$$-\frac{dC_B}{d\tau_A} = \frac{CA}{\frac{R_o(1-XB)^{1/s}}{D a_s} + \frac{1}{k_s a_s} + \frac{1}{k_r a_s}} \quad (14)$$

In this connection:

$$C_A = C_{AO}(1-x_A)$$

When equation (15) in the differential, obtained:

$$dC_A = -C_{AO}\,dx_A \quad (16)$$

Substitution of equation (15) and (16) into equation (14), along with the location settings, resulting in:

$$-\frac{dx_A}{d\tau_A} = \frac{1-x_A}{\frac{R_o(1-X_B)^{1/s}}{D a_s} + \frac{1}{k_s a_s} + \frac{1}{k_r a_s}} \quad (17)$$

Furthermore, if equation (12) in differential, then the result is inserted into equation (10) together with equation (12), (13), and (15), is obtained:

$$-\frac{dx_B}{d\tau_A} = \frac{(1-x_A)(1/R')}{\frac{R_o(1-X_B)^{1/s}}{D a_s} + \frac{1}{k_s a_s} + \frac{1}{k_r a_s}} \quad (18)$$

With :

$$R' = \frac{4/3\pi\, N_{rt}\, \rho_B\, R^3 o}{V C_{AO}} \quad (19)$$

Equation (17) and (18) simultaneously solved numerically by Runge-Kutta method. To calculate the value of k_L, k_s, and k_r is used minimization by Hooke-Jeeves (Jenson and Jeffreys, 1977).

In order to ensure a decisive step, need to see the value of k_L and k_s values, then compared with a value of k_r.

If mass transfer is a step that determines the course of the reaction, the value of k_L, and K_s is much smaller than the value of k_r.

If the chemical reaction is a step that determines the course of the reaction, then the value of k_r is much smaller than the value of k_L or k_s. Thus, equation (17) becomes:

$$\frac{dx_A}{d\tau_A} = k_r (1-x_A) \quad (20)$$

And after the set and integral, obtained:

$$-\ln(1-x_A) = k'\tau_A + b \quad (21)$$

With :

$$K'_r = k_r a_s \quad (22)$$

So equations (21) is quasi-first order reaction equation. In this study the reaction kinetics will be studied and some influential variables.

HOW TO RESEARCH

Raw material research is bittern, which is taken from PT Garam, Kalianget, Madura. Once analyzed, it turns out every liter of bittern containing 48.98 g of magnesium, 40.1 g of calcium, 203.02 g chloride, 3.64 g of sulfate, 2.75 g of potassium, pH = 5.1 and its density 1.254 g / cm .

Lime outages purchased from Jaya Makmur Chemical stores, Surabaya, with the composition: 72.11% active CaO, 73.37% total CaO, 1.19% Mg, 2.34% Fe2O3 + Al2O3 mixture, 2.14% SiO2, 0 , 86% SO3, 0.43% moisture content and the egg passes 170 mesh sieve.

Air used for mixing is obtained by pressing the outside air using a compressor.

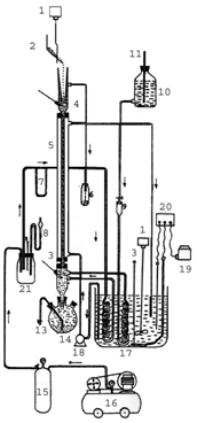
Composition tools can be seen in Figure 1. The reactor is made of glass pipes with a diameter of 2.4 cm and height 144 cm. Inside the reactor there is a serrated plastic barrier mounted oblique criss-cross. As the heating reactor, used hot water flowing in the sheath made of a glass column.

At first the bittern reactor filled with approximately three-quarters in height, followed by bubbling air with a certain speed. Furthermore, the bittern is dripped from the bottle feed and then go to the bottom of the reactor and lime put with its feeder vibrates at certain speeds anyway. Periodically taken samples from the overflow. After steady state is reached, the process continued 10-20 minutes, then stopped.

Analysis of liquid samples to determine levels of magnesium do not react in a way that the volumetric wear Titriplex III (Merck E.)

Variables studied included the speed of air flow, temperature, mole ratio of $Ca(OH)_2$-$MgCl_2$, and initial concentration of magnesium chloride.

ISBN 978 – 979-98623-1-0



1. Stirrer motor
2. Lime Feeder
3. Thermometer
4. reactor connection with lime feeder
5. Reactor
6. bottle container of liquid samples
7. Air Flowmeter
8. Manometer
9. measuring speed of fluids
10. bittern feeding bottle
11. capillary pipe
12. connecting the reactor with a three-neck flask
13. expenses suspension
14. three-neck flask
15. air tank
16. Compressor
17. Thermostat
18. Circulation Pump
19. Powerstat
20. Thermostat relay
21. Stabilizing air flow

Fig. 1. Series of tool-making magnesium hydroxide

RESULTS AND DISCUSSION

Effect of air velocity (G)

The influence of air flow velocity is presented in Table 1. At fixed air flow velocity, increasing the residence time of fluid in the reactor increase the conversion, because the opportunity for $MgCl_2$ to attack the $Ca(OH)_2$ bigger. In addition, increased air flow velocity, flow velocity at a fixed bittern, also increases the conversion, because the more perfect mixing of the reagent substance.

K, much smaller than the value of k_L or k_s. Thus, the chemical reaction is a step that determines the course of the reaction.

K_L relationship with G, as shown in figure 2 a line, can be expressed as:

$$k_L = 0{,}2766\ G^{0{,}0191} \qquad (23)$$

with $\pm$ 1.1% error results.

In figure 3 a line, painted k_s relationship with G which is a curved line with the equation:

$$K_S = 0{,}0415\ G^{0{,}1712} \qquad (24)$$

with $\pm$ 0.98% error results.

Effect of reaction temperature (T)

Table 2 shows that as the temperature increases, the conversion of magnesium chloride (xA) decreases. This is due to the increasing solubility of $Mg(OH)_2$, but reduced the solubility of $Ca(OH)_2$ when the temperature increases.

From table 2 seem k_r value is much smaller than the value of K_L or k_s, so that proved that the chemical reactions that control the speed of the process of formation of $Mg(OH)_2$. With regard to the evidence that the chemical reactions that locate the bad speed the process of formation of $Mg(OH)_2$ and by equation (21), then the chemical reaction that occurs is a quasi-order chemical reaction.

If -ln and $10^3/T$ made a graph (figure 4 rows b) obtained a straight line, and after the change, the equation becomes:

$$K_r = 1{,}1259\ e^{-2992{,}45/RT} \qquad (25)$$

By storing the results of the study 1.45%. Thus, activating energy and frequency factor values of each 2992.45 cal / gmol and 1.1259 to 1.

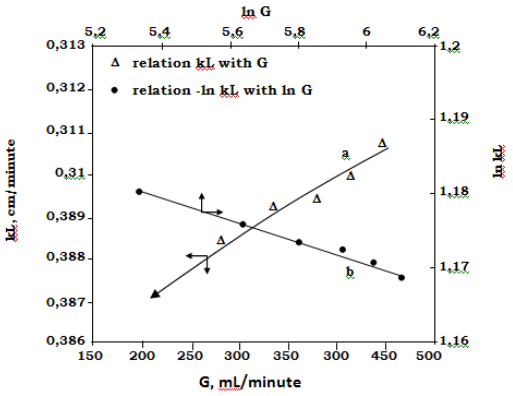


Fig. 2. Relation between k_L with G

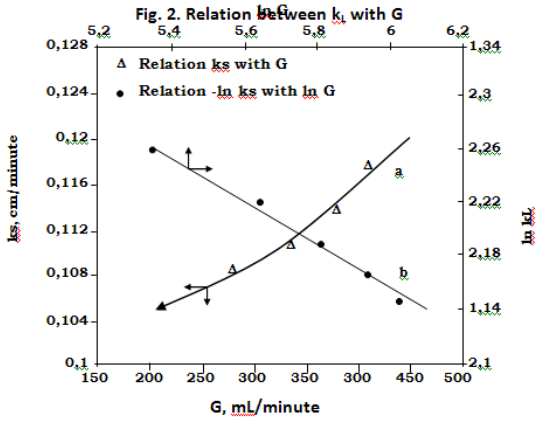


Fig. 3. Relation between k_S with G

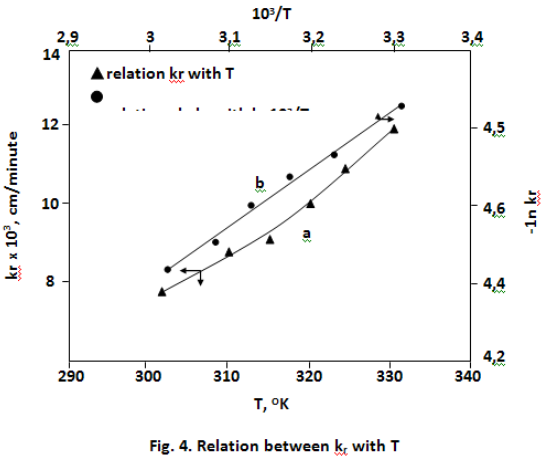


Fig. 4. Relation between k_r with T

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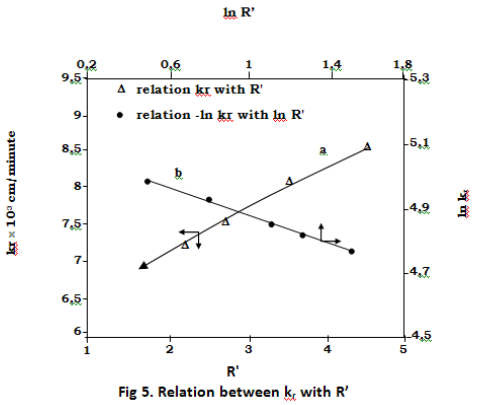

Fig 5. Relation between k_r with R'

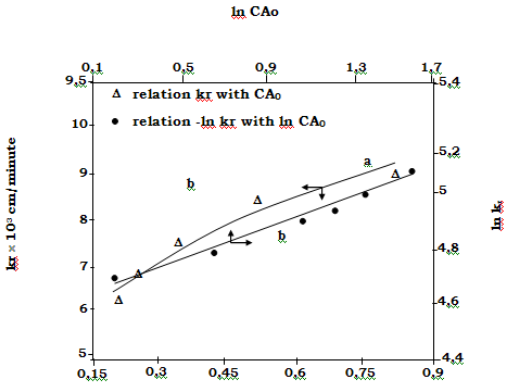

Fig 6. Relation between k_r with C_{A0}

Effect of mole ratio of $Ca(OH)_2$-$MgCl_2$ (R')

Increasing mole ratio of $Ca(OH)_2$-$MgCl_2$, while the residence time remains fluid, causing the conversion of magnesium chloride increases, because the collisions between the molecules of a substance more reagents (see Table 3). K_r values are always smaller than the value of k_L or k_s, so it proved again that the chemical reactions that set the pace. Figure 5 a line, which depicts the relationship between k_r with R ', forming a curved line with the equation:

$$K_r = 0{,}0062\ (R')^{0{,}2074} \qquad (26)$$

With a ± 0.80% error results.

Effect of initial concentration of magnesium chloride (C_{AO})

The results of the experiment influence initial concentration of magnesium chloride are shown in Table 4. At the speed of same liquid feed stream, the conversion increased with increasing initial concentration of magnesium chloride, because the number of moles of magnesium chloride per mole of $Ca(OH)_2$ more, so the greater the possibility of collisions.

Apparently, the value of k_r is smaller than the value of k_L or k_s. Thus, the effect of initial concentration of magnesium chloride, chemical reaction was the one who controls the speed of formation of $Mg(OH)_2$.

From figure 6 the line a, the graph k_r with CAO are curved lines, and the painted $-\ln k_r$ with the $-\ln C_{AO}$, there are points that close to one straight line. Empirical relationship that can be written by equation:

$$kr = 0{,}0097\ C_{AO}^{0{,}2582} \qquad (27)$$

Error outcome trials in equation (27) reached 3.94%.

Combined influence variable

By way of least squares, form combined effects of temperature, mole ratio of $Ca(OH)_2$-$MgCl_2$, and initial concentration of magnesium chloride to kr, can be expressed as:

$$kr = 1{,}4762\ (R')^{0{,}1874}\ (C_{AO})^{0{,}250}0\ e^{-3125{,}0165/RT}$$

Experimental results with errors of equation (28) of ± 2.88%.

CONCLUSION

From the research has been done can be concluded:

1. The speed of the reaction between magnesium chloride into bittern with lime outages controlled by chemical reactions.
2. Chemical reactions that occur of quasi-first order.
3. Reaction rate constants have exponential relationships with temperature and log-log relationship with a mole ratio of $Ca(OH)_2$-$MgCl_2$ and initial concentration of magnesium chloride.
4. A relatively good state of the process is achieved at the speed of the airflow agitator 281 mL/min, 302°K temperature, mole ratio of $Ca(OH)_2$-$MgCl_2$ about 3, and initial concentration of magnesium chloride 0.34 mg mol / mL. In these circumstances $MgCl_2$ conversion reached 89.17%

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